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TANNING EXTRACTS FROM CANAIGRE ROOTS

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CONTENTS

ABSTRACT

Canaigre-root characteristics influencing the recovery of tanning extract are discussed. Pilot-plant data for extraction of the dried or green roots with water and with dilute isopropyl alcohol are presented and compared. Preparation of tanning extract from canaigre roots by extraction with dilute isopropyl alcohol followed by sulfiting gave the largest "tannin yields" yet attained from canaigre. Cost estimates indicate that a process of this type will give the best possibility of producing tanning extract from canaigre roots at a cost competitive with foreign materials. These production costs are considerably lower than could be obtained with water extraction by any process studied in the pilot plant, but the potential profit appears inadequate for a commercial enterprise under present market conditions. The sulfited solvent extract is expected to be less versatile in use than water extracts of canaigre would be.

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by

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INTRODUCTION

This research on the use of canaigre as a tanning extract was carried out as a part of a project to find and develop domestic vegetable tannin sources which can compete economically with foreign materials or which could be used in an emergency when foreign materials are unavailable.

With the passing of the last two large commercial producers of chestnut extract during 1955, the United States heavy leather industry has become almost entirely dependent on foreign sources for vegetable tanning materials (1)*. Today, our annual volume of imports is equivalent to about 125,000 tons of 100% tannin. This situation was forecast when the chestnut blight annihilated our most important domestic source of tannin during the first 25 to 30 years of this century (3).

Concern over our disappearing domestic supplies became magnified during the two World Wars when leather production experienced tremendous increases and when shipping was a major problem. The Department of Agriculture took active interest in the development of domestic vegetable tannins in 1940 when Frey and Sievers (12) described a general program for the investigation of domestic tannin-bearing plants. The lines of work have followed two courses, the utilization of waste barks from the lumbering industry and the study of the possibility of cultivating crop-type tannin-bearing plants. Rogers and Russell reviewed this program in their preliminary report on canaigre (22). Work on Florida scrub oaks (6), Tennessee Valley oak slabs and cord wood (25), and eastern and western hemlock barks (19,20,24) has been reported. Of these the hemlock barks seem to have the greatest chance for successful use because of their availability and higher tannin content. Unfortunately, these raw materials are not generally centered near existing extraction facilities, and transportation costs today prohibit long hauls of these low-valued raw materials.

Studies on the use of native sumac have been published (7,8,14,23). This work shows the possibilities of replacing foreign sumac with an

* Numbers in parentheses refer to literature cited at end of publication.

acceptable domestic extract, but again it is doubtful that this product could be economically competitive in today's markets.

Much of the work carried out at this Laboratory has been on the development of canaigre roots as an annual crop-type source of tannin. Rogers and Russell reviewed the history of canaigre use in their preliminary report (22).

The Crops Research Division of the Agricultural Research Service, United States Department of Agriculture, worked on the agronomic problems of growing and methods of storing the roots for year-round operations. A systematic study of the extraction of tannin from canaigre roots has been made. Cordon et al. (10) reported the difficulty of extracting tannin from canaigre due to the high starch content and the necessity of extracting at a relatively low temperature to prevent starch gelatinization. Luvisi et al. (15,16) showed an increase in tannin yield and purity by extracting with mixtures of organic solvents and water at temperatures well below the starch gelatinization temperature. Reports on pilot-plant investigations of both continuous countercurrent (17) and countercurrent stationary vat leaching (18) systems showed the desirability, yieldwise, of a solvent-water extraction system.

Actual wearing test on a small-scale tannage (4) showed the wear of shoe soles tanned with a blend containing 25% chestnut, 25% sulfited quebracho, and 50% canaigre tannin recovered by water extraction was equal to the wear of comparable soles tanned with a blend of 50% chestnut and 50% sulfited quebracho.

CANAIGRE ROOT CHARACTERISTICS

Canaigre (Rumex hymenosepalus Torr.) is native to Southwestern United States, growing wild in well-drained, sandy soils. Its growth habits have been described (22,26). A typical plant is shown on the cover of this publication. The tuberous roots, which contain the tannin along with considerable amounts of sugar and starch (21), show tremendous variations in composition and extraction characteristics among strains. They may be divided roughly into two groups; a "yellow" group whose root flesh is yellow to orange-brown and a "red" group whose whitish to light-pink roots turn reddish when exposed to the air. In the wild state the red roots occur predominantly west, and the yellow roots east, of the Continental Divide in New Mexico and west Texas. The red roots average much higher in tannin and purity than the yellow roots and have far better extraction characteristics. The yellow roots can be propagated from seeds, but the best varieties of red roots so far studied must be propagated by planting root crowns in order to maintain their desirable characteristics. While crown planting is the more expensive method, it has the advantages of giving considerably larger and more dependable root yields per acre. Since it is currently considered entirely impractical to process yellow root strains, for the most part only red cultivated roots are considered in this work.

HARVESTING AND STORAGE

For highest tannin content and purity the roots should be harvested during the hot summer months after the tops have died and the plants are dormant. For much of the work reported the roots were shredded and air-dried in the sun on concrete strips at harvest. The most practical commercial method appears to be a mechanical drying in a rotary alfalfa-type drier using a lower air temperature than is required for alfalfa (13). The green roots, which are quite durable, can be held for a month or more at room temperature without perceptible loss of tannin, and for much longer periods under refrigeration at 50° F. At a lower refrigeration temperature the purity of the green roots was observed to drop somewhat in a few months, probably owing to the change of some insoluble starch into soluble sugars; but no tannin loss was observed. Simple pit storage by burying the roots in bulk under a layer of earth has been quite satisfactory in some tests, and this may be a good, cheap storage method. During pit storage there was some loss of solids as a result of metabolism of carbohydrates, but no net tannin loss was observed. Thus pit storage increased the purity and tannin content of the roots. The Crops Research Division is continuing storage tests at Mesa, Ariz.

PROBLEMS IN EXTRACTION OF CANAIGRE TANNIN

Extraction of canaigre presents somewhat different problems than are normal with most commercial tannin raw materials because of its high starch content. At the usual extraction temperatures with water, near boiling, the starch gels, forming a sticky impervious mass through which the extractant cannot flow, and the liberated tannin and starch tend to combine to form an insoluble complex which precipitates out and is lost. These actions are greatly reduced at temperatures below about 120° F. Also, the canaigre tannins are of the catechol type, which tend to deposit sludge unless sulfited. Dilute organic solvents, such as acetone or isopropyl alcohol, are generally able to redissolve the "tannin" from the various sludges.

ANALYSIS OF CANAIGRE TANNIN

Since hot-water extraction was found impractical, warm-water extraction for a longer period was used for several years as an analytical procedure, although it gave somewhat erratic results. Later, Luvisi and Rogers (16) developed a more reproducible analytical extraction procedure wherein the tannins are extracted from the roots with 50% aqueous acetone, the acetone is distilled off from the extract, and the remainder is analyzed by the official A.L.C.A. (American Leather Chemists Association) tannin analysis method (2). Reports of the tannin content of canaigre were 20% to 28% higher when analyzed by acetone extraction than when analyzed by the exhaustive warm-water extraction procedure. Thus the maximum extractable tannin by water is only 78% to 83% of that reported by the acetone assay. Moreover, about 15% of this water-extractable tannin, which remains in dilute solution during the official A.L.C.A. analytical method and is absorbed by the hide powder, will not remain in solution and penetrate a hide at the higher concentrations generally used for tanning leather. This leaves the actual usable tannin by water extraction at only 66% to 71% of that reported by the acetone assay.

The solvent method of analysis, however, does not give a true picture of the usable tannin in the canaigre roots either, because all of the "tannin" so extracted will not remain in solution and penetrate a hide at the high concentrations normally used in tanning leather. There is a tendency for canaigre tannin to deposit sludge freely (5); hence, even if the extraction procedure used yields the higher percentage of tannin shown to be present by acetone assay, this material will not be suitable for use directly in tanning. It can, however, be sulfited, much as quebracho extract is, to solubilize the insolubles and prevent precipitation during tannage. Sulfiting, of course, limits the use of the extract in blends of other than sulfited tanning materials.

The highly diluted solutions specified in the official method of determining insoluble solids were not realistic for canaigre extracts. These extracts contain much material that would remain in such dilute solutions but would precipitate from the more highly concentrated solutions used for tanning unless the extracts were sulfited. Hence the insoluble solids values reported in this paper were determined at concentrations of about 40 gm. per liter (10 times the concentration specified in the A.L.C.A. method), which is more nearly representative of actual tanning concentrations

The purity* of the extract recovered from canaigre roots depends upon the methods of extraction and processing as well as the roots from which the extract is produced. The water-extract purity can be raised by fermentation of the extracts to remove sugars (9,11).

EXPERIMENTAL RESULTS

A number of experimental procedures have been studied in the pilot-plant at this Laboratory in a search for the most economical and practical method for recovering the tanning extract from canaigre roots on a commercial scale. The results reported here are probably conservative because better strains of roots may be established soon. The Crops Research Division has already produced small plantings of canaigre roots containing well over 40% tannin (acetone extraction).

Continuous Countercurrent Extraction with Water. More than 10 tons of dry extract was produced for test purposes by a semiworks process based upon the continuous countercurrent water-extraction process reported earlier (17) but modified to use cultivated roots and to reduce the residual insolubles in the extract. Willcox roots, mixed red and yellow strains, which had been propagated from seed, shredded, and air-dried by the Crops Research Division, were extracted in the semiworks plant. Typical equilibrium data for 3 semiworks runs on the earlier crops of Willcox roots, which were mostly red, are given in Table I. (Results on later crops were much poorer because the yellow root fraction increased with reseeding.) In the semiworks process stones were removed from the shredded dried roots by air flotation, then the roots were rehydrated to about 25% moisture to reduce fines, and cut to pass through 1/8-inch holes on a Fitzpatrick Model D comminuting machine ** with sharp knives. They were then extracted with water at 115° F. in a stainless steel Kennedy-type continuous countercurrent extractor, shown in Figure 1.

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* Throughout this paper, purity is defined as $\frac{\text{TANNIN}}{\text{SOLUBLE SOLIDS}} \times 100$

** The mention of commercial products and companies anywhere in this paper does not imply that they are endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned

Table I

Typical Pilot-Plant Data on Warm-Water Extraction of Canaigre Roots[1] by Using a Kennedy-Type Continuous Countercurrent Extractor

[Roots rehydrated to about 25% moisture, cut through 1/8 inch Contact time: 88 minutes; extraction temperature: 115° F.]

Item	Run 27	Run 29	Run 30	Average
Feed rate, lb./hr., M.F.B.	65.2	63.5	58.2	----
Solvent ratio (water in extract/ solids feed)	11.4	11.2	12.8	11.8
Head liquor				
Tannin,%	1.56	1.53	1.42	----
Purity,%	55.4	55.2	55.6	----
Tannin yield, % fed(acetone)[2]	66.0	63.0	67.7	65.0
Tannin yield, % fed(water)[3]	79.4	76.9	81.9	79.4
50% concentrate[4]				
Purity,%	63.87	62.39	65.36	----
Insoluble solids, %[5]	1.24	0.71	0.34	----
Tannin yield, % fed(acetone)[2]	49.4	47.7	56.2	51.1
Tannin yield, % fed(water, settled)[6]	70.2	65.8	79.8	71.9
Dried extract				
Purity,%	64.29	62.36	65.67	----
Insoluble solids, %[5]	0.45	-	0.69	----
Tannin yield, % fed(acetone)[2]	47.1	44.6	56.7	49.5
Tannin yield, % fed(water settled)[6]	67.0	62.4	80.5	70.0

1 Air-dried, shredded Willcox roots grown 2 years from seed.

2 Based on analysis of roots by acetone extraction (16) which averaged 28.6% tannin, M.F.B., and 66.3% purity.

3 Based on analysis of roots by warm-water extraction, which averaged 23.6% tannin, M.F.B., and 60.1% purity.

4 After fermenting, partial concentration, settling and concentration.

5 Measured at 10 times the concentration used in the official A.L.C.A. method.

6 Based on the water-extractable tannin which will remain in the solution after settling at 30° Barkometer, averaging 20.2% tannin, M.F.B., and 57.2% purity.

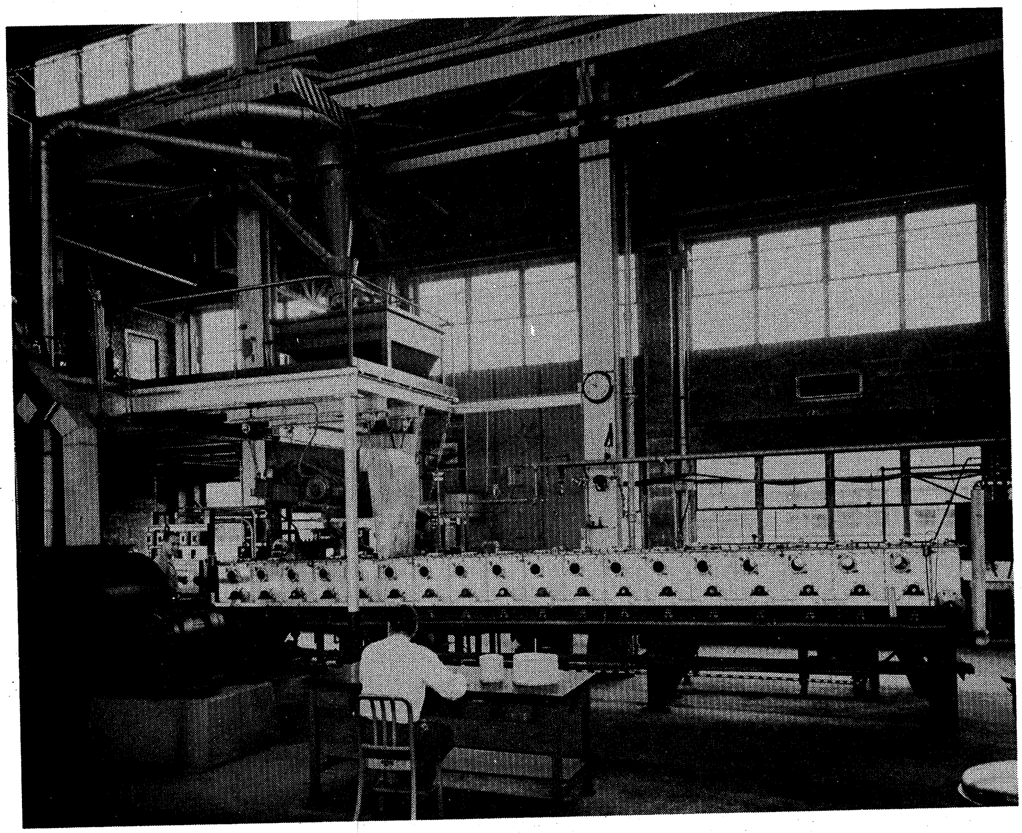

Figure 1

Kennedy-type semiworks countercurrent extractor for warm-water extraction of canaigre

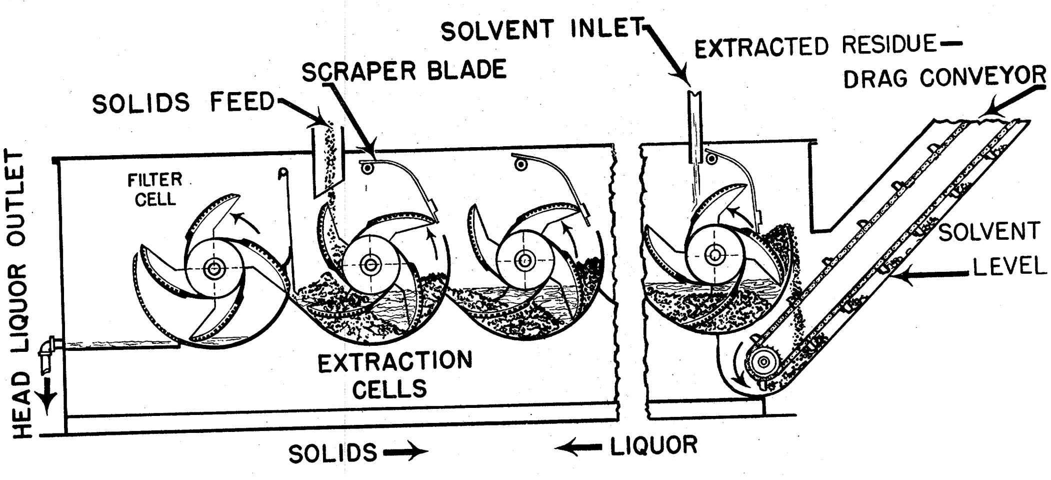

Figure 2

Operation of Kennedy-extractor. (Drawing represents specifically the pilot plant unit shown in Fig. 4, but principle of operation is same for the semiworks unit shown in Fig. 1.)

This extractor consists of a series of 18 semicylindrical cells (16 extraction and 2 filter cells, each 24 by 16 inches long) separated by perforated weirs and arranged so that the extractant flows by gravity through each in series. Each cell is equipped with a paddle wheel having 4 slotted blades which rotate in the semicylindrical trough conveying the solids over the weirs into the next cell countercurrent to the flow of extractant as shown in the operating diagram of a smaller pilot-plant unit, Figure 2. Under the conditions used for most tests, both Kennedy-type units were calculated to be equivalent to about 4 transfer units (number of ideal equilibrium stages in countercurrent series from each of which the liquid leaving the stage is the same composition as the liquid adhering to the solids leaving the stage).

The extracts were clarified in a continuous solid-bowl centrifuge, pasteurized continuously at about 180° F., fermented aerobically with a special strain of *Aerobactor aerogenes* to remove sugars and thereby improve purity, clarified in a Sharples supercentrifuge to remove bacterial debris, concentrated to 30° Barkometer solids, allowed to stand overnight at about 65° F. to precipitate "insolubles" which were soluble at the extraction temperature, recentrifuged through the Sharples supercentrifuge, vacuum evaporated to 50% solids, and finally spray dried.

This process recovered about 50% of the tannin assay by acetone extraction or 70% of the tannin which can be extracted with water and will remain in solution at 7%-8% solids concentration (30° Barkometer). This yield cannot be greatly increased by better extraction since 15% to 20% of the available tannin is lost during fermentation and sludge entrainment, exclusive of mechanical losses. The dried tanning extract produced in these runs had an average purity of 62.7% based on soluble solids.

Countercurrent Batch-Screening Process. Extraction was also studied by a countercurrent batch-screening method which permitted longer contact times and a greater number of theoretical contacts than were possible in the semiworks extractor. The extraction unit, Figure 3, consisted of 5 or fewer 55-gallon, open-top, stainless-steel drums equipped with hot-water heating coils, agitators, transfer pumps, and 2 vibrating screens which could be used as desired to separate the liquid and solids from any cell. Experimental data obtained in this pilot-plant are listed in Table II.

The roots used were of the Salt River strain, a red variety which has been successfully reproduced from crowns by the Field

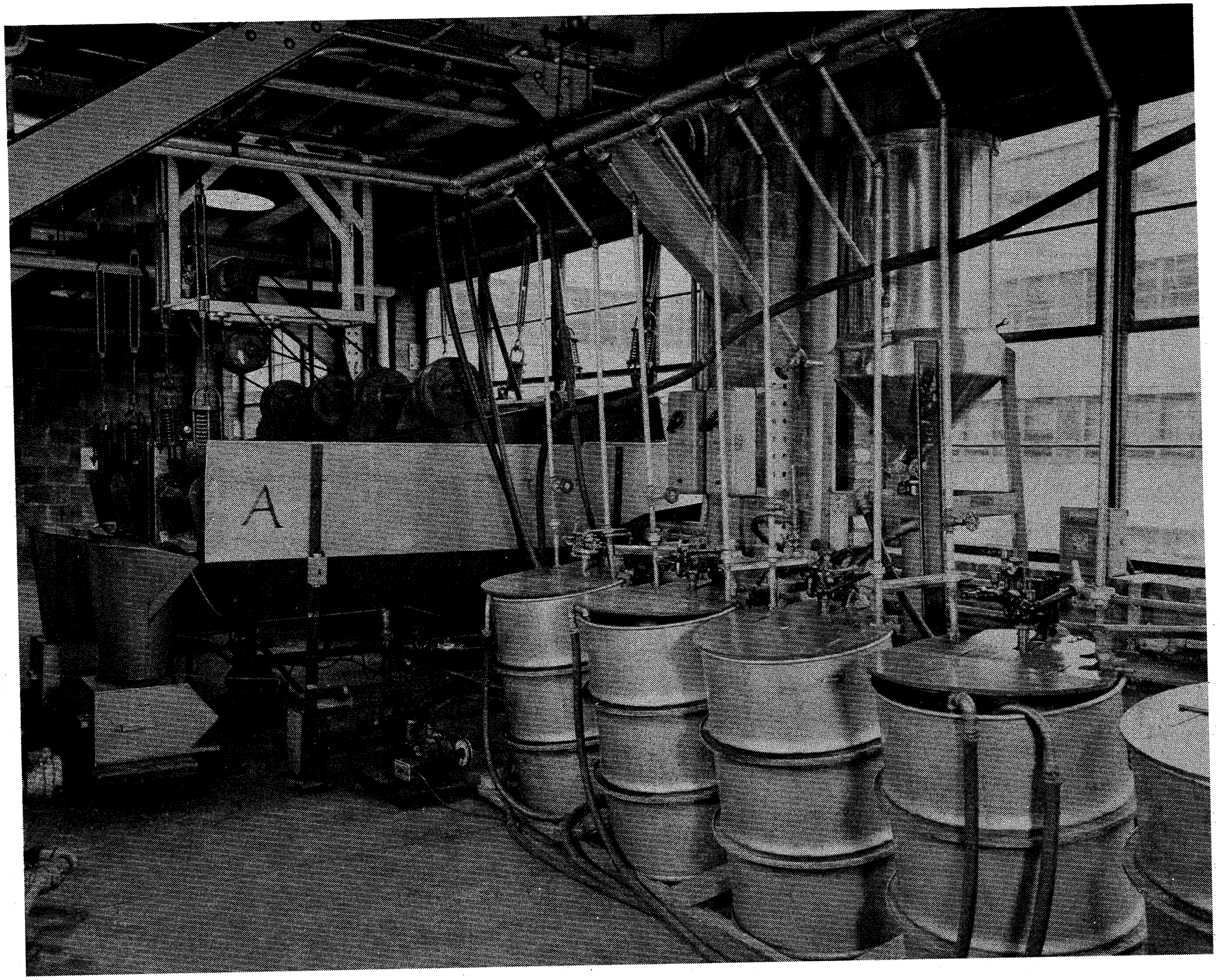

Figure 3
Unit for canaigre extraction by countercurrent batch screening

Table II

Pilot-Plant Data on Warm-Water Extraction of Canaigre Roots[1] by Countercurrent Batch Screening
(Extraction Temperature 118° F.)

Item	Run 2	Run 5	Run 3	Run 4	Run 6	Run 7	Run 8
Contact time, min./cell	120	90	60	30	30	30	30
Contacts, number	11	11	11	7	5	5	5
Equilibrium batches collected, number	6	6	4	4	5	10	12
Solvent ratio (water in extract/solids fed)	6.4	6.5	7.5	7.2	6.9	6.1	6.7
Head liquor							
Purity, %	49.4	52.7	53.0	51.7	54.2	52.9	53.3
Tannin yield, % fed (acetone)[2]	53.4	57.2	64.3	67.0	62.9	59.5	62.8
Tannin yield, % fed (water)[3]	65.7	70.3	79.0	82.4	77.3	73.2	77.2
50% concentrates							
Not settled or fermented							
Purity, %	51.3	-	53.2	-	-	-	-
Tannin yield, % fed (acetone)[2]	53.4	-	62.1	-	-	-	-
Insoluble solids, %[4]	4.1	-	3.9	-	-	-	-
Settled,[5] not fermented							
Purity, %	51.4	50.5	-	-	51.7	-	-
Tannin yield, % fed (acetone)[2]	50.6	48.2	-	[6]63.5	53.1	-	-
Insoluble solids, %[4]	1.7	2.6	-	-	1.7	-	-
Settled,[5] fermented							
Purity, %	58.4	61.1	63.5	62.5	62.7	60.0	60.1
Tannin yield, % fed (acetone)[2]	46.6	41.3	49.8	49.6	50.7	50.4	47.2
Insoluble solids, %[4]	0.7	1.7	1.2	1.7	2.5	3.2	1.3
Tannin yield, % fed (water, settled)[7]	67.5	59.9	72.2	71.9	73.5	73.0	68.2

1 Air-dried, shredded, Salt River roots cultivated 1 year from crowns.

2 Based on analysis of the roots by acetone extraction (16), which averaged 35.9% tannin, M.F.B., and 63.0% purity.

3 Based on analysis of roots extracted with warm water, which averaged 29.2% tannin, M.F.B. and 56.7% purity.

4 Measured at 10 times the concentration used in the official A.L.C.A. method.

5 Allowed to precipitate overnight at 65° F.

6 This figure estimated from the yield after settling, which was 65.2%.

7 Based on a calculated 24.8% M.F.B. water-extractable tannin content which will remain in solution after settling at 30° Barkometer.

Crops Research Division at Mesa, Ariz. These roots have averaged slightly over 35% tannin (acetone assay) and 62% purity (based on soluble solids).

In these runs the air-dried shreds were extracted countercurrently with water at 118° F. in the batch-screening unit using 10.7 to 16.7 pounds of solids per cell, 5 to 11 countercurrent contacts and a cycle of 30 to 120 minutes per cell. The roots were first presoaked 1 hour with extract from the head cell and then cut to pass through 1/16" holes on the Fitzpatrick comminuting machine with sharp knives. This slurry was then screened over a 150-mesh vibrating screen, the solids being fed into the next cell and the liquor removed for processing. As each cell was screened in rotation the solids were removed to the next weaker cell, where they were mixed with the liquor screened from that cell, whereas the liquor was progressively contacted with the next stronger solids batch. In this manner the number of contacts was equal to one less than twice the number of cells used.

The extract from this unit was centrifuged, pasteurized, and fermented as in the semiworks process. After settling overnight at about 65° F. to precipitate insolubles, it was clarified in a Sharples supercentrifuge, vacuum evaporated to about 50% solids, and spray dried. No concentration was required before settling because the desired concentration was obtained directly from the extractor by using a lower solvent ratio, than that used in the semiworks. Yield values are calculated at the 50% concentrate stage, which should give only slightly higher values than after spray drying since the tannin and purity losses during spray drying are very small. Each extraction condition was run to equilibrium and then 4-12 batches were collected for processing. In several runs aliquot parts of the extract were processed without fermentation or without either fermentation or settling as listed in Table II.

The listed contact time per cell includes 10 to 15 minutes for screening the material. This reduces the overall amount of mixing obtained. The screening itself takes an appreciable part of the time required for the shorter (30-minute) cycles. Tannin yields in the head liquors from the extractor were higher for the shorter extraction cycles. Five or seven contacts with a 30-minute cycle time gave about the best yield considering both tannin in head liquor and in dried extract. It is noted that tannin in head liquor varied somewhat more than overall yield of tannin, which suggests that the tannin lost by excessive holding times would be largely lost during settling and fermentation in any case. The

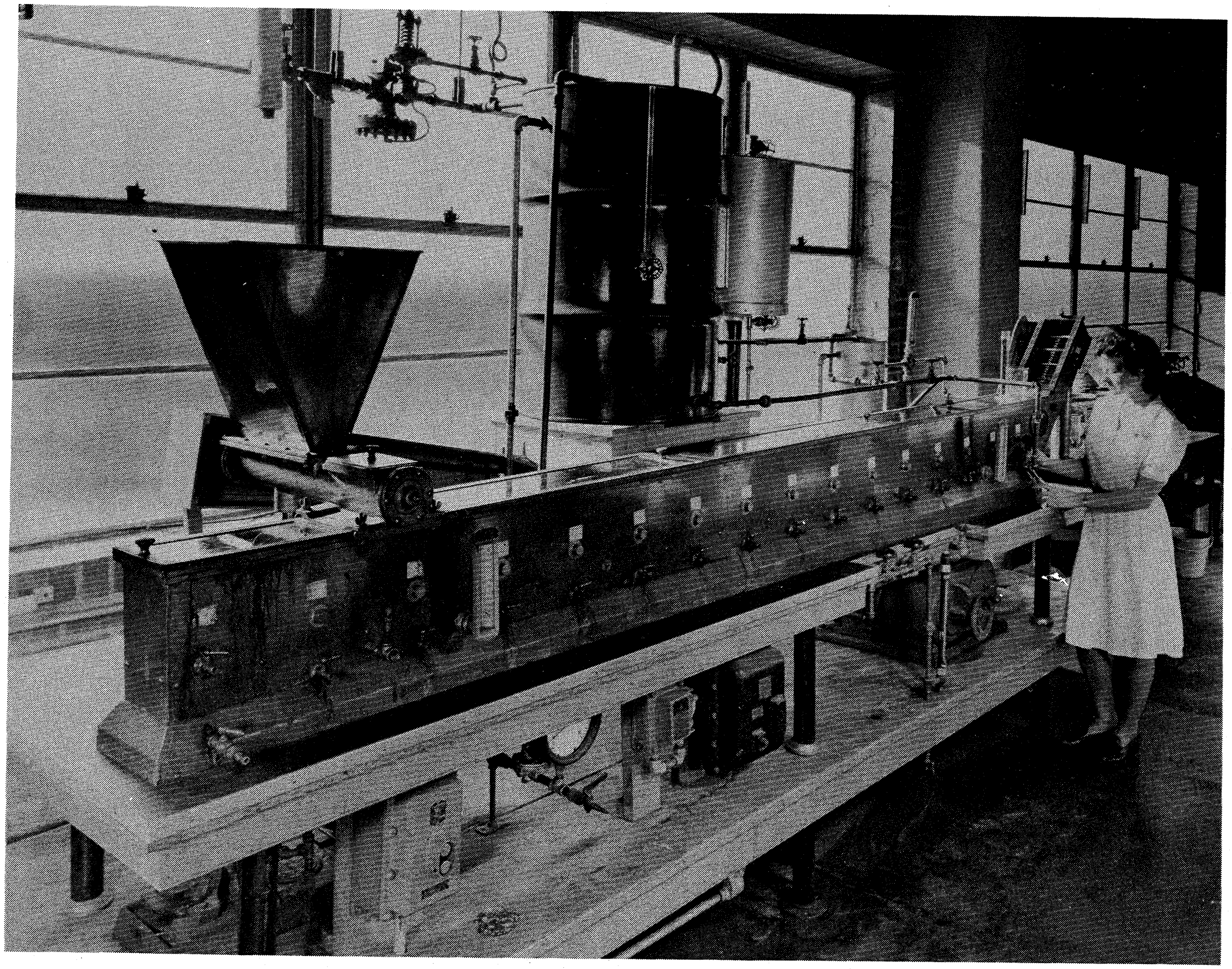

Figure 4
Pilot-plant Kennedy-type extractor used for dilute isopropyl alcohol extraction of canaigre

approximately 50% overall yield of tannin obtained in the extract (based on acetone assay) is almost exactly the same as that obtained in the semiworks. No great increase could be anticipated in either case by longer or more numerous contacts.

Dilute Isopropyl Alcohol Extraction. As will be discussed below, both the continuous and batch experiments in the pilot-plant indicated that warm-water extraction of canaigre tannin could not be done commercially at a profit under prevailing conditions. Following these experiments, some studies were made on solvent extraction of both green and dried Salt River canaigre roots. The apparatus used was a small laboratory Kennedy-type extractor shown in Figure 4. Its operation, the same in principle as that of the semiworks extractor used in the larger-scale warm-water extractions, has already been described (see Fig. 2). The small extractor has 14 extraction cells and 1 filter cell, each 6 inches wide by 8 inches long with perforated transfer paddles. Studies on the same unit were reported by Rieder et al. (17). Like the semiworks extractor, it gave extraction equivalent to about 4 transfer units under the conditions used. The paddles are perforated instead of slotted. Desirable operating conditions as determined by previous work on dry roots were used in these tests. Extraction data are shown in Table III. The dilute isopropyl alcohol readily extracted substantially all of the tannin indicated by the acetone assay from either dried or green roots at a purity close to that of the roots which were used. Previous tests on dried roots have shown no advantage in using concentrations over about 30% isopropanol (by volume), but the yield and purity are somewhat reduced if less than 20% is used. The exact concentration is not very critical. Higher solvent strengths are required with green roots in order to obtain the desired extract composition after dilution by the moisture in the roots; the exact composition depends also upon the solvent ratio used.

This solvent-extracted tannin, however will not tan leather satisfactorily, because it penetrates the hide too slowly and tends to precipitate a high proportion of sludge. Removal of material precipitated at a concentration of 30° Barkometer when held at 65° F. overnight as described for the water-extraction processes, reduced the average yield of tannin in the 50% concentrate from approximately 97% to 81.2% of that in the roots fed (acetone assay) but did not improve the tanning qualities sufficiently to permit practical use in conventional tannages although the nominal insoluble solids were reasonably low.

Extraction of green roots with somewhat higher alcohol concentrations to compensate for the root moisture gave substantially

TABLE III

Pilot-Plant Data on Isopropyl Alcohol Extraction of Canaigre Roots[1] Using a Laboratory-Scale Kennedy-Type Extractor

Item	Shredded, Air-Dried Roots[2]	Green Roots[3]					
	Runs 82-91[4]	Run 174	Run 99	Run 100	Run 101	Run 104	Run 105
Storage of roots							
Condition	Room	Cold	Cold	Pit	Pit	Cold	Cold
Time, months	10	1	1	6	6	2	2
Analysis of roots							
Tannin, %, M.F.B. (acetone)	35.3	37.3	35.9	41.8	37.4	35.7	36.1
Purity, %	62.5	56.7	58.4	63.8	61.6	54.0	53.7
Extraction conditions							
Isopropyl alcohol, % (by vol.)	30	0 (water)	35	35	35	47	47
Temperature, °F.	110	115	110	110	110	110	110
Extraction time, min.	120	120	120	120	120	85	85
Solvent ratio (isopropyl alcohol/solids fed)	11.1	10.9	11.7	12.1	10.9	5.1	6.1
Root feed rate, lb./hr., M.F.B.	2.01	1.44	1.84	1.94	2.07	3.75	3.55
Head Liquor							
Purity, %	62.4	49.1	58.4	64.8	63.0	55.6	55.7
Tannin yield, % Fed (acetone)	96.4	[5]70.2	110	103.0	102.9	102	103.9
50% concentrate							
Purity, %	58.9	-	60.1	-	63.3	[7]54.2	
Tannin yield, % fed (acetone)	81.2	-	100.4	-	104.0	[7]101.3	
Insoluble solids, %[6]	1.2	-	4.9	-	5.8	[7]3.9	
Dried extract							
Purity, %	59.3	-	-	-	-	-	
Insoluble solids, %[6]	1.2	-	-	-	-	-	

1 Grown one year from crowns.
2 Cut on a Ball and Jewel cutter.
3 Cut on a Fitzpatrick comminuting machine.
4 Average of 8 extractions concentrated and dried in 4 batches. Settled over-night at 30° Barkometer and 65° F.
5 Equivalent to about 86.2% of the tannin analysed by water extraction.
6 Measured at 10 times the concentration used in the official A.L.C.A. method.
7 These data were obtained on the combined concentrate from runs 104 and 105.

complete tannin recovery after concentration to 50% solids, but the insolubles remained high even when low solvent ratios were used. The green roots used in these tests were from a single lot which had an average purity of 61.5% when received but which showed a gradual drop in purity during cold storage to about 55% after 2 months.

Sulfiting Extracts. Since solvent extracts of canaigre are not suitable for direct use in tanning hides, sulfiting was considered as a means of modifying the extract to improve hide penetration and reduce sludge formation. In Tables IV and V are shown the results of a series of sulfiting tests on 50% concentrates of tannin extracted from dried or green Salt River canaigre roots by dilute isopropanol, evaporated to remove the isopropanol, then dried, either directly (Table IV), or after settling to reduce the insoluble solids content (Table V). The concentrates were sulfited by heating with sodium bisulfite for various periods of time at temperatures just below boiling. The sulfiting was done with continuous agitation in a jacketed 10-gallon stainless-steel tank or in a 5-liter glass flask on a steam bath.

The "tannin" content by the A.L.C.A. method increased with sulfiting in each case more than could be accounted for by the simple addition of sulfite. The increase varied widely, but averaged about 13% for typical 8-hour runs. This tannin increase on sulfiting also occurs with quebracho (27). The purities increased with time of sulfiting, and were all higher than those of the corresponding original concentrates except in one series under run 97 (Table IV) where excessive sodium bisulfite was used. The insoluble solids were all reduced to a permissible 2% or less when the equivalent of at least 3.5% SO_2 was used for 8 hours or longer. In the case of the air-dried roots the insoluble solids remained a little high, but were reduced when the concentrates were settled and dried (Table V, run 96) Thus with dried roots the extracts would have to be settled either before or after sulfiting. The green roots, on the other hand, offer an advantage in that their insoluble solids are low even without settling. Hence, in their use the expense of both root drying and low-temperature settling and clarifying (which always result in about 15% loss) is eliminated. Furthermore, the green roots give the highest tannin yield (well over 100%) when solvent extraction is used. Where insufficient SO_2 was used (run 103 and part of run 97) the insolubles were high, and increased further with lengthened treatment periods.

A small-scale laboratory tanning test using the sulfited extract from Blend 1 (settled extract from dried roots) alone showed rapid penetration of the hide and little sludge formation. The leather

Table IV

Effects of Sulfiting on 50% Concentrates of Solvent-Extracted Canaigre Tannin

Root conditions	Sulfiting: Concentration (equiv. SO_2[2]), % of solids	Sulfiting: Time, hr.	Purity %: Before Sulfiting	Purity %: After Sulfiting	Purity %: After Drying	Insoluble Solids %[1]: Before Sulfiting	Insoluble Solids %[1]: After Sulfiting	Insoluble Solids %[1]: After Drying	Tannin increase after sulfiting %
Air-dried									
Blend 1[3]	3.1	8	59.3	61.0	-	1.3	0.4	-	8.1
Run 96	3.8	22	61.9	67.4	-	7.9	3.9	-	22.7
Green									
Run 103	2.8	8	56.6	59.6	59.9	5.1	2.7	2.7	8.8
	2.8	12	56.6	62.0	61.8	5.1	3.6	5.7	10.7
Run 98	3.6	4	62.5	61.7	-	8.4	2.8	-	4.5
	3.6	8	62.5	63.2	63.3	8.4	0.9	0.6	8.6
Run 99	3.8	8	60.1	61.5	61.5	4.9	0.9	2.3	11.3
Run 102	4.1	8	56.5	59.7	61.0	4.2	1.6	1.1	15.8
	4.1	12	56.5	61.5	63.1	4.2	-	0.1	16.8
Run 105	4.3	24	54.2	64.0	64.0	3.9	0.8	2.0	30.2
Green pit-stored									
6 months									
Run 101	4.1	8	63.4	65.4	65.6	11.7	1.3	1.6	13.5
Run 97	2.5	10.5	63.8	66.5	-	7.9	4.3	-	17.6
	2.5	17	63.8	68.6	-	7.9	9.3	-	18.8
	2.5	24	63.8	68.5	-	7.9	16.6	-	13.0
	4.9	7	63.8	64.0	-	7.9	1.1	-	16.6
	4.9	13.5	63.8	66.1	-	7.9	0.8	-	21.7
	7.9	5	63.8	60.1	-	7.9	0.5	-	13.7
	7.9	8	63.8	62.1	-	7.9	0.0	-	20.6
	7.9	15	63.8	62.3	-	7.9	2.0	-	18.5

1 Measured at 10 times the concentration used in the official A.L.C.A. method.
2 Added as $NaHSO_3$.
3 Blend of runs 83, 86, 89, and 93. Settled overnight at 30° Barkometer and 65° F., then dried before sulfiting.

Table V

Effects of Settling[1] on Solvent-Extracted and Sulfited Canaigre Tannin 50% Concentrates

Item	Air-Dried roots (Run 96)	Green roots (Run 98)	Green roots, pit-stored 6 months (Run 97)
Concentration of solvent (equiv. SO_2[2]), % of solids	3.8	3.6	4.9
Time of sulfiting, hr.	22	8	13.5
<u>Purity, %</u>			
Before sulfiting	61.9	62.5	63.8
After sulfiting	67.4	63.2	66.1
After drying	-	63.3	-
After settling and concentrating	66.2	62.4	65.6
After settling and drying	65.1	-	65.0
<u>Insoluble solids, %</u>			
Before sulfiting	7.9	8.4	7.9
After sulfiting	3.9	0.9	0.8
After drying	-	0.6	-
After settling and concentrating	0	0.6	1.5
After settling and drying	1.62	-	0.4
<u>Tannin increase, %</u>			
After sulfiting	22.7	8.6	21.7
After settling and concentrating	6.2	[3]-1.4	6.0

1 Settled at 30° Barkometer and 65° F overnight.

2 Added as $NaHSO_3$.

3 Minus sign (-) indicates loss.

yield, however, was low, as would be expected for a sulfited extract used alone. On the other hand, sulfited unsettled extracts gave appreciable sludge formation and slower penetration. The best conditions for sulfiting these extracts, or for using the the sulfited extracts to tan hides, have not been determined, but some modification of the "tannins" in canaigre roots is essential if they are to be recovered cheaply enough and in sufficient quantity and quality for commercial use. For the solvent extraction of canaigre tannin, our work suggests the use of an 8-hour treatment at 210° F. with sodium bisulfite added equal to 3.5% SO_2. Turley and Cronin (27) consider this a low level for bisulfiting quebracho.

DISCUSSION

The results of these semiworks runs and laboratory pilot-plant trials indicate that a solvent-extraction procedure is preferable to a water-extraction procedure for obtaining tannin from canaigre roots. They further indicate that water extraction is not commercially feasible, even with a number of modifications to the procedure used in these runs to improve its efficiency and reduce its cost.

Preparation of Roots for Extraction. Regardless of the method of extraction used, drying of the roots is prohibitive from a cost standpoint. These studies have shown that green roots, even by water extraction, give a somewhat higher yield than air-dried roots (see run 174, Table III). Where the green roots cannot be extracted immediately, some inexpensive method of bulk storage appears feasible

The cutter used for most of the roots processed in this study is not believed satisfactory for a production unit because the roots do not pass through its openings readily. In one set of tests a grater-type rasp like that used to prepare potatoes for the manufacture of potato starch was much more efficient. This grater was a 5/8-inch-diameter pilot-plant model which gave an excellent cut at a high relative capacity without clogging.

Modifications to Water-Extraction Process. There are two steps in the semiworks process which could be profitably eliminated. One of these is evaporation before precipitation of insolubles, a step which would be unnecessary if sufficient theoretical stages were used in the extractor to permit recovery of the extract in a more highly concentrated state. The other step is fermentation to remove the sugars. This appears to be impractical since its results are quite variable and since it raises the purity only slightly (from about 53 to 60%) and causes a substantial loss in tannin. Only a slight tannin loss was evident from analysis of the liquors immediately before and after fermentation, but in the subsequent clarification step the fermented extracts lost much more tannin by sedimentation, giving a net reduction in yield from 62% to 50% of the tannin in the roots based on acetone analysis. Hence fermentation, along with the pasteurization and centrifugation that were done in the semiworks runs both before and after this step, could be eliminated from the process if a product of 53% purity were acceptable.

Even with these changes, however, which would be expected to increase the tannin yield by almost one-quarter and appreciably reduce raw-materials cost, water extraction of canaigre tannin would not be economical.

COST ESTIMATE ON SIMPLIFIED WATER-EXTRACTION PROCESS

Cost estimates have been computed based on a continuous countercurrent mixing and screening process of water extraction with 6 cells and 6 screens, all operating continuously. In this process, slurry would be pumped continuously from each cell to a screen, the filtrate passing to the next stronger cell and the slurry passing to the next weaker cell or discarded. Here only one contact would be obtained per cell and the effective number of transfer units would be slightly reduced for the same number of cells, but operations would be much simpler than in the batch screening process used in the pilot-plant. Breaks in the cycle between cells would be eliminated so that effective mixing time in the cells would be greater for the same cycle time than in the batch unit. For operating economy a sufficiently low solvent ratio would be used so that the extract would be about 30° Barkometer and could be cooled to 65° F. and settled without an intermediate concentrating step. The clarified extract would then be concentrated to about 50% solids and spray dried without fermentation. This simplified process is estimated to recover about 62% of the tannin in the roots (acetone assay) in the form of a dried extract of about 52% purity containing about 1% insoluble solids and 3% water.

Detailed cost estimates comparable to the one for solvent extraction cited hereafter show that a plant to produce 8,030 tons per year of this product (4,000 tons per year of pure "tannin") would cost about $1,050,000 and the "cost to make" would be about 11.4 cents per pound of product (19.3 cents per pound of pure "tannin") not including profits or management costs for growing the roots, sales costs, profits, or income taxes on the extract. A 5% interest on fixed capital is included in the "cost to make". This "cost to make" is far too high to compete with foreign tannin sources at present even if this low purity product were found acceptable.

Some increase in yield could be gained by sulfiting the extract, but it would not be great enough to justify limiting the use of tannin to a sulfited extract. Use of the Kennedy-type extractor would increase the cost by about one-third and give only minor savings in utility and labor costs.

This highly simplified water-extraction process is still uneconomical. It is unlikely that any water-extraction process producing acceptable canaigre tannin can be economical unless new root strains of much superior quality are developed or the commercial value of tanning extracts rises considerably.

COST ESTIMATE ON SOLVENT-EXTRACTION PROCESS

Of the various possible canaigre tannin recovery methods which have been studied here, a process consisting of dilute isopropyl alcohol extraction of green roots followed by sulfiting of the tannin in water solution appears to have the greatest chance of being commercially feasible. This process gives the highest yield and is the simplest of the various processes considered which give products of reasonably high purity and low insolubles. Figure 5 gives a flow diagram of this process for a plant calculated to produce dried extract of 62% purity containing 1%-2% insoluble solids and about 3% moisture. The tannin yield, 38 pounds of sulfited tannin per 100 pounds of root solids, is about 8.5% more tannin than can be shown to be in the roots by acetone assay, but this results from the action of the bisulfite.

Root Storage and Preparation. During the months June through September the roots can be harvested and used directly. The roots themselves are quite durable, and if not excessively "cooked" by sun exposure no special storage conditions would be required for at least another month. Roots for the remaining 7 months of operation would require special storage. Some method of bulk storage is believed most practical for this purpose, although no actual recommendation can be made now. For the cost estimate which follows later, storage is assumed to be in piles, 20 feet long by 6 feet deep covered over with about 2 feet of earth.

The roots to be extracted must be washed to remove extraneous material which may damage the cutter. They would then be finely cut or shredded in a grater-type rasp.

Extraction. In this process extraction would be carried out in a continuous countercurrent extractor such as the Kennedy apparatus used for the pilot-plant studies. Mixing and screening

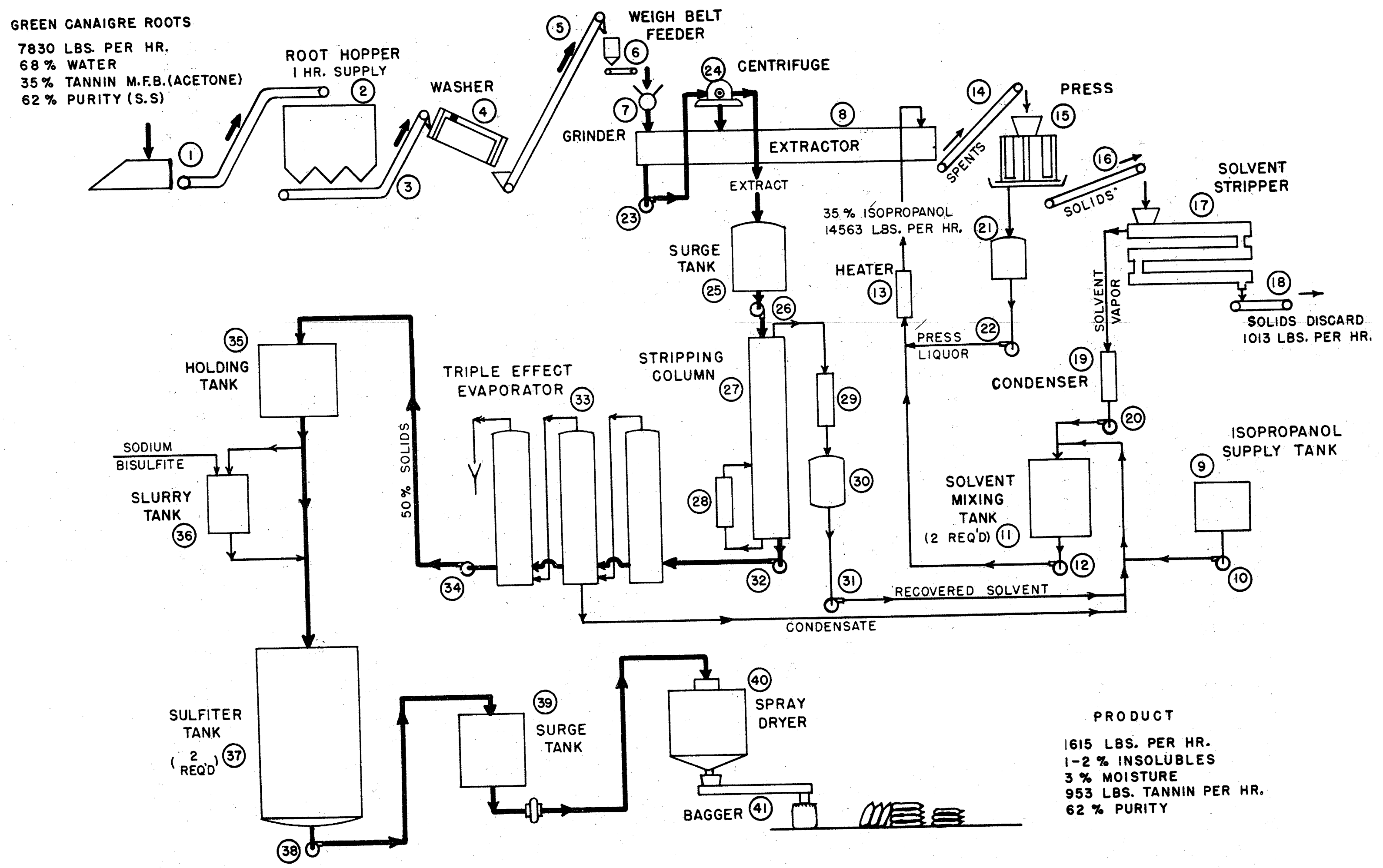

Figure 5
Flow diagram for production of sulfited tannin extract from green canaigre roots

equipment such as suggested for water extraction would not be advantageous; such a unit would have to be vaportight for safety and for conservation of solvent, and should be much smaller than that used for water extraction owing to the higher yields and extractive capacities obtainable with solvent. If the extractor has 5 transfer units, operates at 110° F., and uses as solvent 5.8 parts of 35% isopropyl alcohol (by volume) per part of solids in the green roots fed, then it is calculated that 98% of the tannin in the roots (by acetone analysis) would be extracted in the head liquor. These are about the most economical conditions under which canaigre roots can be extracted considering evaporation costs, yield, extractor cost, etc.

Variation of the solvent concentration or temperature would affect the yield to some extent, but these factors are not extremely critical. Lower yields and purities result at lower temperatures and solvent concentrations.

The alcohol-saturated spent roots would be pressed and steam-stripped primarily to recover the solvent for reuse.

Solids collected from the head liquor in the centrifugal clarifier are primarily entrained material which can be expected to go out with the spents and not to build up excessively in the extractor.

Concentration and Sulfiting. A solvent stripping column for isopropanol recovery may not be required, if a short rectifying column is added to the vapor line from the spents stripper before condensing. Such a column would be very economical to operate, because the alcohol is already in the vapor state. In any case water equivalent to that in the green roots must be discarded during concentration and drying.

As previously noted the results obtained by sulfiting vary with the sulfiting time and amount of sulfite used. The process shown here is based on sulfiting a 50% solution for 8 hours at about 210° F. with 6% sodium bisulfite based on extract solids. This should increase the "tannin" by about 12% and greatly reduce sedimentation during tannage.

The sulfited extract can then be spray-dried directly. This was accomplished routinely in the pilot-plant. Such an extract, however, is expected to be less versatile in use than a water extract would be.

Costs. A cost estimate was made for this dilute-solvent extraction process based on a plant to produce 6,780 tons of dried sulfited extract (containing 4,000 tons of pure tannin) per year as shown in the flow diagram, Figure 5. Circled numbers represent item numbers in the equipment summary.

This estimate assumes that the root storage facilities and processing plant are to be a new and independent enterprise located in the Mesa, Ariz. area. The canaigre roots would be grown nearby under contract and delivered at the plant during the 4 months from June to September. The Field Crops Research Division, which has been studying propagation of these roots, at Mesa, estimates* that growing and hauling these roots to the plant during the June to September harvest season would cost about $10.27 per ton of green roots at 70% moisture. This cost does not include profits or management costs for the grower or the cost (paid by the extractor) of storing sufficient roots for use during the October to May period. Extraction plant operation is assumed for 350 days per year, 24 hours per day but roots would be removed from storage only 8 hours a day.

An equipment summary is given in Table VI. The capital costs are summarized in Table VII, and production costs are listed in Table VIII. The total fixed capital is estimated at $921,850. The cost to make of 14.2 cents per tan unit (extract containing 1 pound pure tannin) does not include the root grower's management costs or profits, or any extract selling costs or profits, but it does include a 5% interest charge on fixed capital. Allowing a selling expense equal to 10% of sales and an additional 12% of fixed capital for profits, the price would be 19.2 cents a tan unit, which is a little above the current prices for foreign extract even without allowance for the canaigre grower's profits or management costs. This process might become competitive if roots containing more tannin could be produced at a materially lower cost per tan unit, if the capital costs could be reduced by use of some pre-existing equipment or facilities, or if tannin prices should rise.

CONCLUSIONS

The canaigre plant does not appear to be practical for commercial development at current market prices for tanning extracts, although sulfited solvent extract would not be far out of line costwise. Canaigre remains, however, a potential domestic source of vegetable tanning extract which could be grown as an annual crop in an emergency where cost would not be the major factor. Fundamental information on the composition of canaigre roots, which makes them act differently from other tannin sources during extraction and tanning which influences sulfiting of the extracts, is still incomplete.

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* PRIVATE COMMUNICATION

Table VI

Equipment Summary for Production of Canaigre Tannin
by Solvent Extraction Process

Item No.[1]	Description	Price	Item No.[1]	Description	Price
1	Discharge pit and conveyor	$ 4,610	22	Pump, 10 gal. per min., bronze	$ 350
2	Root storage bin, 25' x 20' x 10', 16 hr.	2,870	23	Pump, 30 gal. per min., bronze	500
3	Belt conveyor, 18" wide x 38' long	2,850	24	Solid bowl continuous centrifuge	15,430
4	Washer, rotary barrel type	1,870	25	Tank, 1200 gal.	1,600
5	Belt conveyor 18" wide x 38' long	2,850	26	Pump 28 gal. per min.	500
6	Weigh belt feeder, 7830 lb. per hr.	2,550	27	Stripping column, 26" dia., 10' packing	1,520
7	Grater-type rasp	2,330	28	Reboiler, 95 sq. ft.	900
8	Kennedy-type extractor, 20 cells	87,520	29	Condenser, 98 sq. ft., copper	660
9	Solvent tank, 10,000 gal.	1,960	30	Tank, copper, 200 gallons	370
10	Pump, 10 gal. per min., bronze	350	31	Pump, 8 gal. per min., bronze	350
11	Solvent mixing tanks, lined, 13,000 gal., 2 required	9,300	32	Pump, 22 gal. per min., bronze	500
12	Pump, 20 gal. per min., bronze	450	33	Evaporator, triple effect, 642 sq. ft.	23,500
13	Heat exchanger, 15 sq. ft., bronze	170	34	Pump, metering, bronze	370
14	Screw conveyor, 6" dia. x 15' long, s.s.	3,040	35	Tank, wood, 200 gal.	520
15	Continuous press 8440 lb. per hr.	9,580	36	Tank, wood, 100 gal., with agitator	450
16	Screw conveyor, 6" dia. x 15' long, s.s.	3,040	37	Sulfiters, 2300 gal., 316 s.s., 2 required	17,750
17	Solvent stripper	6,650	38	Pump, bronze, 60 gal. per min.	620
18	Waste conveyor, screw, 6" x 30', steel	1,560	39	Tank, wood, 2000 gal.	520
19	Condenser, 34 sq. ft., copper	280	40	Spray drier, 1445 lb. water evap., per hr.	32,700
20	Pump, turbine type bronze	250	41	Bagger, 1615 lb. per hr., in 100-lb. bags	630
21	Tank, 250 gal., copper	580			
				TOTAL	$244,400

1 ITEM NUMBERS CORRESPOND TO CIRCLED NUMBERS ON FLOW DIAGRAM (FIG. 5).

Table VII.

Capital Costs for Production of Canaigre Tannin by Solvent Extraction Process

Land and site preparation	$ 12,500
Roads and parking areas	18,100
Railroad siding	18,000
Buildings	71,300
Boilers	29,800
Equipment - manufacturing	244,400
Erection of equipment - manufacturing	72,850
Instrumentation	6,100
Piping and ductwork	48,900
Erection of piping and ductwork	34,200
Lighting, installed	3,100
Power, installed	24,200
Transportation facilities	28,000
Insulation	5,700
Freight on equipment	4,900
Office furniture and fixtures	3,700
Trenches for pit storage	20,700
Spray pond	3,250
Contingencies	92,200
Engineering fees	138,300
Contractor's fee	36,900
Fire protection and safety	4,800
Total fixed capital	921,900
Working capital	267,000
Total capital	$1,188,900

Table VIII

Cost Sheet for Production of Canaigre Tannin by Solvent Extraction Process

Item	Cost per day	Cost per lb. of dried extract	Cost per lb. of tannin
	Dollars	Cents	Cents
1. Material			
Canaigre roots, 94 tons at \$10.95/ton (68% H_2O) (equal to \$10.27/ton at 70% H_2O)	1,029.30	2.66	4.50
Isopropanol, 121.4 gals. at 39¢/gal.	47.35		
$NaHSO_3$, 2160 lbs. at 4.5¢/lb.	97.20		
Total material cost	1,173.85	3.03	5.13
2. Labor	435.60	1.12	1.91
3. Total prime cost	1,609.45	4.15	7.04
4. Indirect materials, 388 bags at 28¢ each	108.64	0.28	0.47
5. Indirect labor:			
Supervision	117.71		
Watchman	17.83		
Mechanics	102.00		
Office help	43.09		
Chemist	20.00		
6. Indirect expense:			
Insurance, public liability and fire	26.34		
Taxes	52.68		
Interest on fixed capital	131.69		
Depreciation	263.38		
Social Security	8.71		
Workmen's Compensation	7.84		
Unemployment Insurance	41.97		
Vacation time	25.24		
Power	36.07		
Steam	116.75		
Water	33.41		
Gas	28.08		
Maintenance, repairs and renewals	152.94		
Gasoline, automotive repairs	15.62		
Factory supplies	22.94		
Laboratory, analytical	25.00		
Waste disposal	34.73		
Miscellaneous factory expense	25.00		
7. Total factory overhead	1,349.02	3.48	5.90
8. Factory cost	3,067.11	7.91	13.41
9. Interest on working capital	38.14		
10. Research and development expense	38.88		
11. Administration and general expense	109.38		
12. Cost to make	3,253.51	8.39	14.22

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